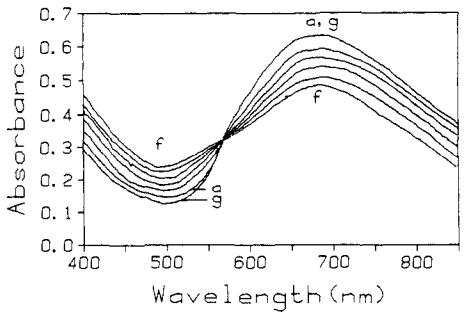
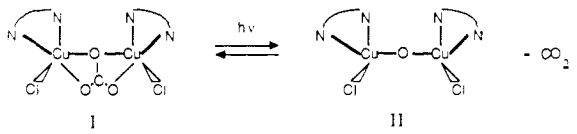


Figure 1. Absorption spectral changes occurring after irradiation of a 1.6×10^{-5} M aqueous solution of I at room temperature. Spectrum a is that of compound I; spectrum f is that of compound II. Spectra g is obtained by flushing photoproduced II with CO_2. Spectra b–e were obtained after irradiation times (min) of 5, 10, 15, and 22, respectively.

Scheme I



Satisfactory elemental analyses were obtained for both of the compounds. The IR spectrum of the carbonato complex contained bands at 1530, 1360, 820, and 750 cm^{-1} characteristic of the bridging "tridentate" carbonate.[1,6]

The electronic absorption spectrum of the μ-carbonato complex in aqueous solution consists of overlapping bands at 250 nm (ϵ = 950 M^{-1} cm^{-1}) and 328 nm (ϵ = 1300 M^{-1} cm^{-1}) and a shoulder at 350 nm. This spectral region contains the chloride-to-copper and the oxo-to-copper charge-transfer bands.[1,6] The electronic absorption spectra of I and II in the 400–850-nm region which are monitored in the photochemical studies are shown in Figures 1 (parts a and f, respectively). Complex I has a broad band at 680 nm with ϵ = 162 M^{-1} cm^{-1}, and complex II has a similar band also at 680 nm with ϵ = 140 M^{-1} cm^{-1}. This similarity suggests that there is no drastic rearrangement of the oxo complex on reaction with CO_2. The 680-nm band is assigned to d–d transitions for two reasons. First, assignment as charge-transfer transitions between the copper and the phenanthroline are eliminated because the analagous μ-carbonato and μ-oxo complexes containing substituted ethylenediammine ligands have a similar absorption band at 700 nm.[1,6] Secondly, d–d bands in the 700-nm region in copper(II) chloride complexes are well known.[1,7] On the basis of breadth of the spectrum, the observed 680-nm band is probably comprised of several closely spaced d–d excited states.

Photochemical reactivity was studied by irradiating a 1.6×10^{-5} M aqueous solution of I at 351.1 nm with an argon ion laser. The photon flux was 2.47×10^{16} photons/s (14.0 mW) measured with a calibrated power meter. All photoreactions were carried out at room temperature in a constantly stirred quartz cell. Absorption changes were measured by using a HP 8451A diode array spectrophotometer.

The spectral changes resulting from photolysis of I are shown in Figure 1. As irradiation proceeded, the absorbance at 680 nm decreased and that at wavelengths below 575 nm increased with an isosbestic point appearing at 575 nm. The concentration changes of I and II were calculated from the measured absorption spectral changes. A plot of the change of the concentration of I versus time was linear for irradiation times up to 22 min and passed through the origin. After longer irradiation times the plot exhibited curvature, and the isosbestic point in the spectra disappeared, both of which are indicative of secondary photolysis. The quantum yield for the disappearance of I and the appearance of II, calculated from the linear portion of the plot, was 0.44 ± 0.07.

The quantum yield for CO_2 loss is very sensitive to the nitrogen donor ligand. When phenanthroline was replaced by tetraethylethylenediamine, for example, the quantum yield decreased to less than 10^{-2}.

Cessation of photolysis at any time in the reaction sequence when the isosbestic point is maintained followed by flushing of the reaction mixture with CO_2 results in the reformation of the μ-carbonato complex. The spectral change is shown in Figure 1. When the system is flushed with CO_2 after prolonged photolysis which has caused loss of the isosbestic point, the spectra show incomplete regeneration of the μ-carbonato complex.

Photolysis of the μ-carbonato complex causes efficient carbon dioxide loss. The μ-oxo photoproduct binds CO_2 to form the starting material in high yield. The photodissociation of CO_2 from the carbonato complex and the thermal association of CO_2 with the μ-oxo copper dimer form a unique system for reversible carbon dioxide binding.

Acknowledgment. This work was made possible by a contract from the Office of Naval Research. We thank Prof. William Kaska for helpful discussions and Kyeong-Sook Shin for technical help.

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"Armed" and "Disarmed" *n*-Pentenyl Glycosides in Saccharide Couplings Leading to Oligosaccharides

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Efficient protocols for building oligosaccharides from monosaccharide components present some of the greatest challenges in organic synthesis, one of which is shown in Scheme I. Thus, combination of **1** and **2** requires that the anomeric substituent, Y, of the alcohol donor **2** be less reactive, under the coupling conditions, than substituent, X, of the glycosyl donor **1**, in order to avoid self-condensation of **2**. The consequence of this is that for further elaboration at the reducing end of the product **3**, the stable substituent, Y, must be replaced with a new activated substituent, X′, in **4**. In the present state of the art, if **3** is a glycoside (i.e., Y = OAlk), the conditions for installation of the activated substituent X′ might affect the newly forged intersaccharide bond and/or the protecting groups R_1, R_2, and R_3. This task becomes increasingly daunting as the concatenation of saccharides grows. Therefore, saccharide coupling methodology could profit from a simple protocol for activating and deactivating the anomeric center of a normal, stable glycoside, X = Y = OAlk. In this manuscript, we describe some recent observations which relate to this need.

We recently reported that *n*-pentenyl glycosides undergo chemospecific cleavage, **6** → **9**, with *N*-bromosuccinimide under conditions that leave a wide variety of other protecting groups unaffected.[2] According to our proposed mechanism (Scheme II), replacement of water with an alcohol, SOH, should lead to glycoside exchange, **6** → **10**, a particularly appealing prospect for the synthesis of higher saccharides, where S = sugar.[3] However,

(1) Financial support of this work was supplied by the National Science Foundation (CHE 8703916) and Glaxo, Incorporated (RTP, North Carolina).

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(3) For the use of *n*-pentenyl glycosides in the formation of a wide variety of disaccharides see: Fraser-Reid, B.; Konradsson, P.; Mootoo, D. R.; Udodong, U. *J. Chem. Soc., Chem. Commun.* **1988**, 823.

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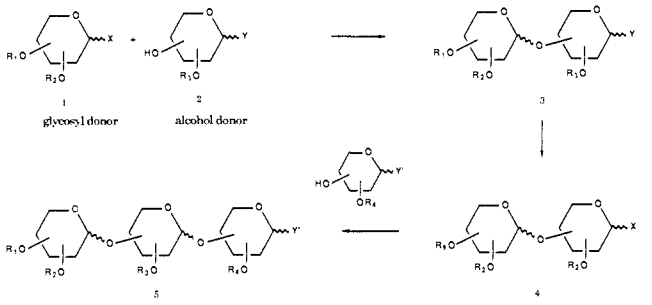
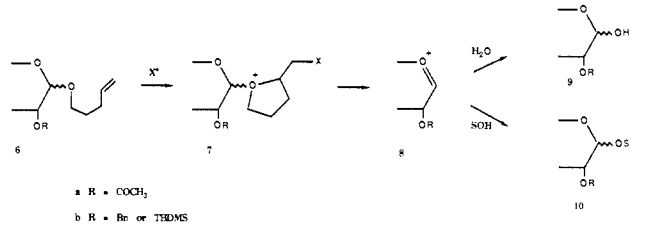
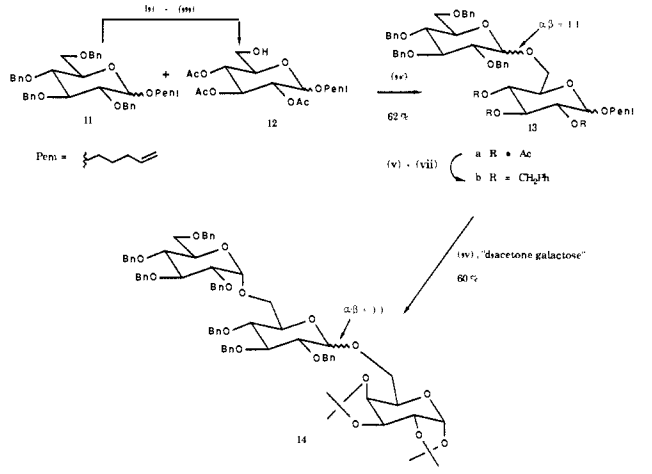
Scheme I



Scheme II



Scheme III[a]

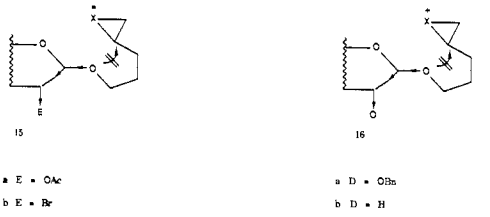


[a] (i) Na, NH_3; (ii) Ph_3CCl, DMF, Et_3N then Ac_2O; (iii) BF_3-OEt_2, CH_2Cl_2–MeOH; (iv) I(collidine)$_2ClO_4$, 2 equiv of CH_2Cl_2; (v) separate; (vi) NaOMe, MeOH; (vii) $PhCH_2Br$, NaH. DMF, $(n\text{-}Bu)_4NI$.

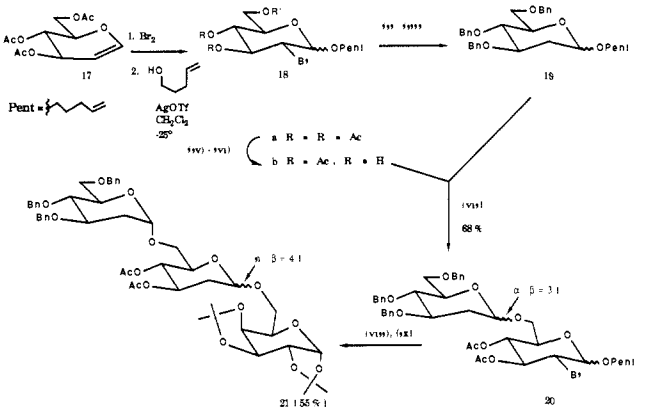
the promise of achieving even greater finesse in this exercise emanated from the observation that an ester (e.g., **6a**) was hydrolyzed much more slowly than an ether (e.g., **6b**). *The latter observations suggested that the pentenyl group could be "armed" or "disarmed" by the type of protecting group placed on the C2 oxygen.*

The foregoing notion was reduced to practice, as shown in Scheme III. Previously described glycoside **11** was processed to give **12** by employing standard transformations. Coupling of **11** and **12**,[4] mediated by iodonium dicollidine perchlorate,[5] afforded a 62% yield of disaccharide **13a**. Therefore, the 2-*O*-acetyl group of **12** had indeed "disarmed" the pentenyl glycoside, thereby

Chart I



Scheme IV[a]



[a] (i) Bu_3SnH, PhH; (ii) NaOMe, MeOH; (iii) $PhCH_2Br$, DMF, NaH, $(n\text{-}Bu)_4NI$; (iv) Et_3N, MeOH–H_2O; (v) Ph_3CCl, Et_3N, DMF, then Ac_2O; (vi) BF_3-OEt_2, CH_2Cl_2–MeOH; (vii) I(collidine)$_2ClO_4$, CH_2Cl_2; (viii) separate, Bu_3SnH, PhH; (ix) I(collidine)$_2ClO_4$, CH_2Cl_2, diacetone galactose.

ensuring that **11** served as the only glycosyl donor. Accordingly, there was no evidence for a hexaacetyl disaccharide arising from self-condensation of **12**.

The anomers of **13a** were separated, and the acetyl groups were replaced with benzyl. The reducing end of **13b** was then "armed" for further coupling, and, indeed, reaction with "diacetone galactose"[6] led to the trisaccharide **14** in 60% yield.

The ability of an ester to disarm the pentenyl glycoside can be rationalized as depicted in Chart I. Thus, it can be assumed that the cyclic halonium ions in **15** and **16** are formed reversibly according to the timely studies of Liotta,[7] and electron density on the glycosidic oxygen is depleted so that nucleophilic attack on the halonium ion is less favored than in the etherified counterpart, **16a**.

This train of thought led us to address the vexing problem of 2-deoxyoligosaccharides. These substances are exceedingly sensitive to acidic media, and in this context the neutral conditions of our oxidative hydrolysis[2] were of particular interest.

A route to 2-deoxyglycosides (Scheme IV), pioneered by Lemieux and Fraser-Reid,[8] involves the haloalkylation of glycals **17** → **18** with subsequent reductive dehalogenation, **18** → **19**. 2-Halogenoglycosides (e.g., **15b**) are similar to the 2-*O*-acetates **15a** with respect to their inductive effects. Hence, compounds **15b** and **16b** should also represent a "disarmed" and "armed" pair of reactants.

This postulate is indeed viable. Thus, the 2-bromoalcohol, **18b**, was coupled with the 2-deoxyglycosyl donor, **19**, to give a 60% yield of **20** with no evidence of self-condensation of **18b**. Radical induced debromination then "armed" the reducing end of **20**, allowing further coupling leading to **21**.[9]

(4) The glycosidation procedure was carried out as follows. Iodonium dicollidine perchlorate (1.5 mmol) was added to a solution in dichloromethane (10 mL per mmol) of the "activated pentenyl glycoside" (1 mmol) and the "deactivated pentenyl glycoside" (1 mmol) and flame dried 4A molecular sieves. When the reaction was complete, as shown by TLC, the mixture was diluted with dichloromethane and filtered through Celite. The filtrate was washed with 10% aqueous sodium thiosulfate, saturated sodium bicarbonate solution, and brine. The solvent was dried ($MgSO_4$), filtered, and evaporated in vacuo. The products were purified by silica gel chromatography.

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(9) An invention disclosure has been filed for the processes described in this communication.